ELECTROPLATING METHOD USING COMBINATION OF VIBRATIONAL FLOW IN PLATING BATH AND PLATING CURRENT OF PULSE

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a plating method, and particularly to a plating method using a specific combination of a physical condition of a plating bath and an electric condition of plating current.

2. Description of the Related Art

An electroplating technique of forming a film of electrically conductive material on the surface of an article has been broadly used in the manufacturing industry of articles such as electronic parts, etc. Particularly, in order to satisfy requirements of miniaturization and high functionality to electronic parts, conductive patterns to be formed on the surfaces (containing the inner surface of through hole, the inner surface of blind via hole) of articles have been required to be formed finely.

For example, the microstructure design of wiring patterns is promoted in connection with decrease of the pitches of input/output terminals due to the high-integration design of semiconductor devices, and in connection with this promotion, it has been required that the through hole and the blind via hole are designed to have an inner diameter of 100 μm or less, further 50 μm or less, still further 30 μm or less. Further, a large aspect ratio of 5 or more, further 8 or more has been required to the through hole and the blind via hole.

For example, in order to reduce the capacity between wires which occurs due to the microstructure design of wires required in connection with the high-integration design, copper wires are used in place of aluminum wires which have been hitherto used, and a damascene method using electroplating to form copper multi-layered wires has been used. In this method, it has been required to perform copper deposition in very small

blind via holes having the inner diameter of 1 μm or less.

Further, it has been required that a pair of electrode films are formed on the surface of a chip part having a dimension of about 0.3mm.

Particularly, the applicant of this application has proposed a plating method that is effectively applicable to articles having microstructured parts such as fine holes, etc. (see JP(A)-11-189880). According to this method, vibrational flow induced in a plating bath and bubbling induced by a diffusing pipe are used in combination. This method is also effectively applicable to electroless plating as well as electroplating.

However, in this method, it is required to dispose the diffusing pipe in a plating tank in which the plating bath is accommodated, and also it is required to establish an air pipe to the diffusing pipe. Therefore, the amount of the plating bath and the dimension of the plating tank must be relatively increased, so that the plating apparatus itself must be designed in large size.

Besides, DC power source is generally used as power source for the electroplating. In order to enhance the quality of plating films, there has been proposed a technique of carrying out plating while the plating current is periodically varied. In this method, positive-polarity current and negative-polarity current alternately flows. That is, a plating film is temporarily formed by supplying the positive-polarity current, and then projecting portions of minute uneven portions on the surface of the plating film thus formed are concentratively and partially melted by supplying the negative-polarity current. The above operation is repeated to achieve a high-quality plating film that has a flat surface and no defects such as minute voids or the like. According to this method, however, the surface portion of the plating film which is temporarily formed is removed and thus this method has a disadvantage in enhancement of the film forming speed (that is, the enhancement of the plating treatment speed).

It is a recent tendency that conductive patterns are designed in a further microstructure design, and when a plating film having such a conductive pattern is formed, defects or unevenness in film thickness is liable to occur. Therefore, it has been more and more difficult to keep the excellent quality of the plating film.

The applicant of this application has also proposed a plating method of carrying out chrome-plating while vibrationally stirring the plating bath, and a plating method of accommodating many articles to be plated (hereinafter referred to as "plating target articles") in a barrel and carrying out chrome-plating while vibrationally stirring the plating bath (see JP(A)-7-54192 and JP(A)-6-330395).

However, these methods use direct current as plating current, and these publications have no specific disclosure on the application of these methods to minute plating target articles such as articles each of which has a width (the dimension in the traverse direction to the longitudinal direction) of 5mm or less, for example, 0.3 to 1.0mm. In the barrel plating process for these minute plating target articles, the plating target articles are overlapped with one another in the barrel, and thus the distribution of plating liquid to desired plating film forming portions of the plating target articles is extremely lowered. Therefore, there are a lot of technical difficulty for these minute plating target articles beyond comparison with plating target articles having relatively large widths, and a further improvement must be made in point of the film forming speed and the evenness of film thickness.

SUMMARY OF THE INVENTION

Therefore, an object of the present invention is to provide a plating method which can form a plating film having a microstructured conductive pattern with high quality so that the plating film has no defect and is not uneven in film thickness.

Another object of the present invention is to provide a plating method which can form a high-quality plating film having a microstructured conductive pattern at high speed.

Another object of the present invention is to provide a plating method which can efficiently form a high-quality plating film having a microstructured conductive pattern by a relatively small apparatus.

In order to attain the above objects, according to the present invention, there is provided an electroplating method, characterized in that a plating target article disposed so as to be in contact with plating bath is set as a cathode while a metal member disposed so as to be in contact with the plating bath is set as an anode, and a voltage is applied between the cathode and the anode while vibrational flow is induced by vibrating vibrational vanes which are fixed in one-stage or multi-stage style to a vibrating rod vibrating in the plating bath interlockingly with vibration generating means, wherein plating current flowing from the anode through the plating bath to the cathode is pulsed and alternately set to one of a first state where the plating current keeps a first value $I1$ for a first time $T1$ and a second state where the plating current keeps a second value $I2$ having the same polarity as the first value $I1$ for a second time $T2$, the first value $I1$ being five or more times larger than the second value $I2$, and the first time $T1$ being three or more times longer than the second time $T2$.

In an aspect of the present invention, the first value $I1$ is 6 to 25 times as large as the second value $I2$, and the first time $T1$ is 4 to 25 times as long as the second time $T2$. In an aspect of the present invention, the first value $I1$ is set to 0.01 to 300 seconds. In an aspect of the present invention, the vibrational vanes are vibrated at an amplitude of 0.05 to 10.0mm and a vibration frequency of 200 to 1500 revolutions per minute. In an aspect of the present invention, the vibrational vanes are vibrated so that the vibrational flow of the plating bath has a

three-dimensional flow rate of 150mm/second or more. In an aspect of the present invention, the vibration generating means vibrates at 10 to 500 Hz.

In an aspect of the present invention, the plating target article is vibrated at an amplitude of 0.05 to 5.0mm and a vibration frequency of 100 to 300 revolutions per minute. In an aspect of the present invention, the plating target article is swung at a swinging width of 10 to 100mm and a swinging frequency of 10 to 30 times per minute.

In an aspect of the present invention, the plating target article has a face to be plated having a microstructure of a dimension of 50μm or less.

In an aspect of the present invention, a plurality of plating target articles are accommodated in a holding container, the holding container having small holes through which liquid of the plating bath is allowed to pass and being equipped with an electrically conductive member which is brought into contact with the plating target articles to make current flow through the plating target articles, and wherein the holding container is rotated around the rotational center corresponding to a non-vertical direction in the plating bath to roll the plating target articles in said holding container to thereby repeat the contact and separation between each of the plating target articles and the electrically conductive member.

In an aspect of the present invention, the width of each of the plating target articles is equal to 5mm or less.

According to the electroplating method of the present invention, even when a plating conductive pattern is minute, a plating film having uniformity in thickness and no defect can be formed with high quality. Further, according to the present invention, a high-quality plating film of microstructured conductive pattern can be obtained at high speed. Still further, according to the present invention, a high-quality plating film of microstructured conductive pattern can be efficiently obtained by a

relatively small apparatus.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a cross-sectional view showing the construction of a plating apparatus to which a first embodiment of a plating method according to the present invention is applied;

Fig. 2 is a cross-sectional view showing the construction of the plating apparatus to which the first embodiment of the plating method according to the present invention is applied;

Fig. 3 is a plan view showing the construction of the plating apparatus to which the first embodiment of the plating method according to the present invention is applied;

Fig. 4 is an enlarged cross-sectional view showing the fixing portion of a vibration transmitting rod to a vibrating member;

Fig. 5 is an enlarged cross-sectional view of the fixing portion of a vibrating vane to the vibration transmitting rod;

Fig. 6 is a diagram showing a modification of the fixing portion of the vibrating vane to the vibration transmitting rod;

Fig. 7 is a cross-sectional view showing a modification of fixing a plating target article to a cathode bus bar;

Fig. 8 is a graph showing variation of plating current flowing through the plating target article;

Fig. 9 is a cross-sectional view showing the construction of a plating apparatus to which a second embodiment of the plating method of the present invention is applied;

Fig. 10 is a cross-sectional view showing the construction of the plating apparatus to which the second embodiment of the plating method of the present invention is applied;

Fig. 11 is a plan view showing the construction of the plating apparatus to which the second embodiment of the plating method of the

present invention is applied;

Fig. 12 is a cross-sectional view showing a plating apparatus used for the embodiment of the plating method of the present invention;

Fig. 13 is a partially-notched plan view of the plating apparatus of Fig. 12;

Fig. 14 is a cross-sectional view showing the fixing of a vibrational flow inducing portion constituting the plating apparatus to a plating tank;

Fig. 15 is a cross-sectional view showing the fixing of the vibrational flow inducing portion constituting the plating apparatus to the plating tank;

Fig. 16 is a plan view showing the fixing of the vibrational flow inducing portion constituting the plating apparatus to the plating tank;

Figs. 17A to 17C are plan views showing a laminated member;

Figs. 18A and 18B are cross-sectional views showing a state that the top portion of the plating tank is closed by the laminated member;

Figs. 19A to 19E are diagrams showing the laminated memeber;

Fig. 20 is a graph showing variation of plating current flowing through a plating target article;

Fig. 21 is a cross-sectional view showing a modification of the vibrational flow inducing portion;

Fig. 22 is a plan view showing the vibrational flow inducing portion of Fig. 21; and

Fig. 23 is a diagram showing an example of a power source for pulse plating.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Preferred embodiments according to the present invention will be described hereunder with reference to the accompanying drawings. In the figures, the members or portions having the same functions are represented

by the same reference numerals.

Figs. 1 and 2 are cross-sectional views showing the construction of a plating apparatus to which a first embodiment of a plating method according to the present invention will be applied, and Fig. 3 is a plan view of the plating apparatus shown in Figs. 1 and 2.

In these figures, reference numeral 12 represents a plating tank, and plating bath 14 is stocked in the plating tank 12. Reference numeral 16 represents a vibrational flow generator or vibrational flow inducing portion. The vibrational flow generator 16 includes a base stand 16a fixed to the plating tank 12 through a vibration proof rubber, coil springs 16b serving as vibration absorption members which are fixed to the base stand at the lower ends thereof, a vibrating member 16c fixed to the upper ends of the coil springs 16b, a vibrating motor 16d serving as vibration generating means fixed to the vibrating member 16c, a vibration transmitting rod 16e fixed to the vibrating member at the upper end thereof, and vibrating vanes 16f fixed to the lower half portion of the vibration transmitting rod so as to be immersed in the plating bath 14. Further, a rod-shaped guide member may be disposed in each of the coil springs 16b as shown in Fig. 12.

The vibrating motor 16d vibrates at frequencies of 10 to 500Hz, preferably 20 to 60Hz, more preferably 30 to 50Hz under the control based on an inverter, for example. The vibration generated by the vibrating motor 16d is transmitted through the vibrating member 16c and the vibration transmitting rod 16e to the vibrating vanes 16f. The tip edge of each vibrating vane 16f vibrates at a desired oscillation frequency in the plating bath 14. The vibration is generated as if each vibrating vane 16f bends from the base portion fixed to the vibration transmitting rod 16e toward the tip edge thereof. The amplitude and frequency of the vibration are different from those of the vibrating motor 16d, and determined in accordance with the dynamical characteristics of the vibration transmission passage and the mutual action characteristics between each vibrating vane

and the plating bath 14. In the present invention, the amplitude is preferably in the range of 0.05 to 10.0mm, for example 0.1 to 10.0mm, and the frequency is preferably in the range of 200 to 1500 revolutions per minute, for example 200 to 800 revolutions per minute.

Fig. 4 is an enlarged cross-sectional view showing the fixing portion of the vibration transmitting rod 16e to the vibrating member 16c. Nuts 16i1, 16i2; 16i3, 16i4 are fixed through vibrational stress dispersing members 16g1, 16g2 and washers 16h1, 16h2 to a male screw portion of the upper portion of the vibration transmitting rod 16e from both the upper and lower sides of the vibrating member 16c. The vibrational stress dispersing members 16g1, 16g2 are formed of rubber, for example.

Fig. 5 is an enlarged cross-sectional view showing the fixing portions of the vibrating vanes 16f to the vibration transmitting rod 16e. Vibrating vane fixing members 16j are disposed at both the upper and lower sides of each of seven vibrating vanes 16f. Further, a spacer ring 16k for setting the interval between the vibrating vanes 16f is interposed between the neighboring vibrating vanes 16f through the fixing members 16j. Nuts 16m which are fitted to male screws formed on the vibration transmitting rod 16e are disposed at the upper side of the uppermost vibrating vane 16f and the lower side of the lowermost vibrating vane 16f.

Fig. 6 is a diagram showing a modification of the fixing portions of the vibrating vanes 16f to the vibration transmitting rod 16e.

In this modification, each vibrating vane 16f is individually fixed to the vibration transmitting rod 16e by nuts 16n disposed at both the upper and lower sides of each vibrating vane 16f. An elastic member sheet 16p formed of fluororesin or fluorinated rubber may be interposed between each vibrating vane 16f and the fixing member 16j to prevent the vibrating vanes 16f from being damaged.

As shown in Fig. 6, the lower surface (press face) of the upper fixing member 16j is designed to have a convex cylindrical shape, and the

upper surface (press face) of the lower fixing member 16j is designed to have a concave cylindrical shape corresponding to the above convex cylindrical shape. Therefore, a part of each vibrating vane 16f which is pressed by the fixing members 16j from the upper and lower sides is bent, and the tip portion of the vibrating vane 16f intersects the horizontal plane at an angle α. The angle α may be set to a value in the range from -30 ° to 30 ° , preferably in the range from -20° to 20 ° . Particularly, the angle α is preferably set to a value in the range from -30 ° to -5 ° or from 5 ° to 30 ° , preferably in the range from -20° to -10° or from 10° to 20 ° . When the press faces of the fixing members 16j are the plane face, the angle α is set to 0° . The angle α is not necessarily equal to the same value among all the vibrating vanes 16f. For example, as shown in Fig. 1, a negative angle value may be set to one or two lower vibrating vanes 16f (i.e., the vibrating vanes 16f are bent downwardly, that is, they are bent in the opposite direction to that of Fig. 6) while a positive angle value is set to the other vibrating vanes 16f (i.e., they are bent in the same direction as that of Fig. 6).

The vibrating vanes 16f may be formed of elastic metal plates, synthetic resin plates or rubber plates. The thickness of each vibrating vane 16f is set so that the tip edge portion of each vibrating vane 16f exhibits a flutter phenomenon (a state as if the vibrating vanes are fluttered). When the vibrating vanes 16f are formed of metal plates such as stainless steel plate or the like, the thickness thereof may be set to 0.2 to 2mm. When the vibrating vanes 16f are formed of synthetic resin plates or rubber plates, the thickness thereof may be set to 0.5 to 10mm.

In Figs. 1 to 3, a swinging motor 20 is connected to a swinging frame 24 through a link rod 22. The swinging frame 24 is disposed so as to be reciprocally movable in the horizontal direction (the right-and-left direction in Fig. 1) on rails 26. A vibrating motor 28 is fixed to the swinging frame 24. Further, a cathode bus bar 30 and an anode bus bar 32

are fixed to the swinging frame 24 while they are kept insulated from the swinging frame 24, and they are connected to a negative-electrode terminal and a positive-electrode terminal of a power source circuit 34. The power source circuit 34 can generate a rectangular voltage from an AC voltage. Such a power source circuit has a rectifying circuit using a transistor and it is known as a pulse power source device.

In the present invention, a circuit for rectifying AC current (containing adding DC components) and then outputting the rectified current is used as the power source circuit (power source device) used to generate plating current. As such a power source device or rectifier may be used a transistor adjustment type power source, a dropper type power source, a switching power source, a silicon rectifier, an SCR rectifier, a high-frequency type rectifier, an inverter digital control type rectifier (for example, Power Master produced by Chuo Seisakusho Co., Ltd.), KTS series produced by Sansha Denki Seisakusho Co., Ltd., an RCV power source produced by Shikoku Denki Co., Ltd., a device which comprises a switching regulator type power source and a transistor switch and supplies rectangular pulse current by switching on/off the transistor switch, a high-frequency switching power source (in which AC current is converted to DC current through a diode, then high frequency of 20 to 30KHz are applied to a transformer to carry out the rectification and smoothing again, and then the output is taken out), a PR type rectifier, a high-frequency control type high-speed pulse PR power source (for example, HiPR series produced by Chiyoda Co., Ltd. or the like.

Here, the current waveform will be described. In order to implement both the increase in plating speed and the improvement of the characteristics of plating films, it is important to select the wave form of plating current. The voltage and current conditions required for the electroplating are varied in accordance with the type of plating, the composition of plating bath and the dimension of the plating tank, and thus

they cannot be sweepingly specified. However, if the plating voltage is set to a DC voltage of 2 to 15V, it can sufficiently cover the whole at present. Therefore, four kinds of rated output voltage of the plating DC current (6V, 8V, 12V, 15V) are standardized in the industry. The voltage below the above rated can be adjusted, and thus a power source for generating a rated voltage which has a slightly extra voltage with respect to a desired voltage value required for plating is preferably selected. In the industry, the rated output current from 500A, 1000A till about 2000A to 10000A are standardized as the rated output current of the power source, and the other current values are provided in the form of production to order. It is better that the required current capacity of the power source is determined as the desired current density of plating target article x the surface area of the plating target article in accordance with the type and surface area of the plating target article, and a proper standard power source satisfying the above required current capacity is selected.

The pulse wave is originally defined as a pulse having a sufficiently shorter width w than its period T. However, this definition is not strict. The pulse wave contains waves other than the square wave. The operating speed of elements used in a pulse circuit is increased, and the pulse width of ns (10^{-9}s) or less can be treated. As the pulse width is smaller, it is more difficult to keep the front and rear edges of the waves sharp. This is because the pulse contains high-frequency components.

A saw-tooth wave, a ramp wave, a triangular wave, a composite wave, a rectangular wave (square wave), etc. are known as the types of pulse waves, and particularly the present invention preferably uses the rectangular wave in consideration of the efficiency of electricity and smoothing.

Fig. 23 shows an example of a pulse plating power source. As shown in Fig. 23, it contains a switching regulator type DC power source and a transistor switch, and rectangular pulse current is supplied to a load by

switching on/off the transistor switch at high speed.

The cathode bus bar 30 is mechanically and electrically connected to the upper portion of an electrically conductive holding member 40 for holding a plating target article X. The lower portion of the plating target article holding member 40 is immersed in the plating bath 14, and the plating target article X is electrically connected to this portion and held by a clamp or the like. As not shown, an anode metal member (for example, which is accommodated in a plastic basket) is mechanically and electrically connected to the anode bus bar 32, and the lower portion thereof is immersed in the plating bath 14. Various well-known methods, shapes and structures may be used as the methods of fixing the plating target article to the cathode bus bar and fixing the anode metal member to the anode bus bar and the shapes and structures of the cathode bus bar and the anode bus bar.

Fig. 7 is a cross-sectional view showing a modification of the fixing of the plating target article to the cathode bus bar. In this modification, the electrically conductive holding member 40 is designed to have a hook portion 40a which is provided at the upper portion thereof and fitted to the cathode bus bar 30, a clamp portion 40b which is provided at the lower portion thereof and pinches the plating target article X, and a compression spring 40c for generating the clamp force of the clamp portion.

In Figs. 1 to 3, the swinging frame 24 and the holding member 40, and further the plating target article X secured to the swinging frame 24 and the holding member 40 are swung at a swinging width of 10 to 100mm and a swinging frequency of 10 to 30 times per minute by actuating the swinging motor 20. Further, the vibrating motor 28 is vibrated at a frequency of 10 to 60Hz, preferably at a frequency of 20 to 35Hz under the control using an inverter, for example. The vibration occurring in the vibrating motor 28 is transmitted to the plating target article X through the swinging frame 24 and the holding member 40, whereby the plating target article X is vibrated

at an amplitude of 0.05 to 5.0mm, for example 0.1 to 5.0mm, and a vibration frequency of 100 to 300 revolutions per minute.

Fig. 8 is a graph showing the variation of plating current (current density) flowing through the plating target article X due to a voltage applied across the cathode bus bar 30 and the anode bus bar 32 by the power source circuit 34.

As shown in Fig. 8, the plating current is shaped to have such a rectangular pulse train that a first state where the plating current keeps a first value I1 for a first time T1 and a second state where the plating current keeps a second value I2 (<I1) for a second time T2 appear alternately. Here, the first value I1 and the second value I2 have the same polarity. I1 is five or more times as large as I2 (for example, six or more times, e.g. six times to 25 times), preferably eight times to 20 times. T1 is three or more times as long as T2 (for example, four or more times, e.g. 4 times to 25 times), preferably six times to 20 times. Such plating current and the vibrational flow of the plating bath 14 caused by the vibrational flow generator 16 are combined with each other, whereby excellent quality and a high film forming speed can be achieved even for the plating of minute conductive structure patterns.

The first value I1 and the first time T1 are properly determined in accordance with the type of plating (for example, copper sulfate plating, copper cyanide plating, copper pyrophosphate plating, nickel plating, black nickel plating, nickel sulfamate plating, chromium plating, zinc cyanide plating, no cyanide zinc plating, alkaline tin plating, acidic tin plating, silver plating, gold cyanide plating, acidic gold plating, copper-zinc alloy plating, nickel-iron alloy plating, tin-lead alloy plating, palladium plating, solder plating or the like), the composition of the plating bath or the like. For example, I1 may be set to a value in the range of 0.01 to 100[A/dm^2], and T1 may be set to a value in the range from 0.01 to 300[Second], e.g. from 3 to 300[Second]. However, these parameters are not

limited to specific values. The optimum I1, I2, T1, T2 may vary in a broad range in accordance with the type of plating, the composition of the plating bath or the like. For example, they may vary due to variation of the composition of the plating bath in the progress of the plating treatment.

The plating bath 14 is selected in the same way as the well-known electroplating method in accordance with a plating film to be formed. For example, in the case of the copper sulfate plating, the following may be used as through hole bath:

Copper sulfate : 60 to 100g/L(liter)
Sulfuric acid: 170 to 210g/L
Brightener: proper amount
Chlorine ion: 30 to 80mL/L

The following may be used as normal bath for the copper sulfate plating:

Copper sulfate : 180 to 250g/L
Sulfuric acid: 45 to 60g/L
Brightener: proper amount
Chlorine ion: 20 to 80mL/L

Further, in the case of the nickel plating, the following may be used as barrel bath:

Nickel sulfate: 270g/L
Nickel chloride: 68g/L
Boric acid: 40g/L
Magnesium sulfate: 225g/L

The following may be used as normal bath for the nickel plating:

Nickel sulfate: 150g/L
Ammonium chloride: 15g/L
Boric acid: 15g/L

The following may be used as Watts bath for the nickel plating:

Nickel sulfate:	240g/L
Ammonium chloride:	45g/L
pH:	4 to 5
bath temperature:	45 to 55℃

Further, in the case of the acidic tin plating, the following may be used as sulfate bath:

Stannous sulfate:	50g/L
Sulfuric acid:	100g/L
Cresolsulfonic acid:	100g/L
Gelatin:	2g/L
β-naphthol:	1g/L

Electronic parts, mechanical parts, etc. may be used as articles X to be plated, and the articles X are not limited to specific ones. The present invention is remarkably effectively applied to a case where a plating film having a microstructure is formed. Particularly, the following cases may be considered as the plating of these articles X: formation of a plating conductive film onto the inner surface of a minute blind via hole or through hole having an inner diameter of 100 μm or less (for example, 20 to 100 μm, or particularly 50 μm or less, further 30 μm or less, e.g. 10μm, 5μm, 3μm, etc.) and having a depth of 10 to 100μm for example in a multi-layered wiring board; formation of a conductive film in a minute groove to form a high-density wiring pattern having a pitch of 50 μm or less (for example, 20 to 50 μm, or particularly 30 μm or less, further 20μm or less, e.g. 10μm, 5μm, etc.), the minute groove having a width of 30μm or less (particularly 20μm or less, further 10 μm or less, e.g. 5 μm, 3μm, etc.) and depth of 7 to 70 μm for example; formation of an embedded conductive film into an extremely minute blind via hole having an inner diameter of about 0.3 μm or less or into an extremely minute groove having a width of 0.1 μm and depth of 1.5μm by copper damascene method when multi-layered wires of a semiconductor device are formed; formation of

minute electrode bumps disposed in a high-density arrangement in a semiconductor device; etc. The improving effect of the present invention is particularly remarkable when it is applied to the structure having a high aspect ratio, for example 3 or more, especially 5 or more.

Further, an extremely small article having an average diameter of 5 to 500μm may be used as the plating target article X. Here, the average diameter is defined as the average value of representative dimensions in the three directions that cross to one another at right angles. As this type of plating target article X may be provided metal powder such as copper powder, pre-treated aluminum powder or iron powder, synthetic resin powder such as ABS resin powder or the like which is treated to have electrical conductivity, ceramic chips which are treated to have electrical conductivity, etc. Further, other electronic parts, mechanical parts, metal powder alloy, minute particulate inorganic/organic pigment, metal balls, etc. may be also provided.

For example, Ni plating films may be formed on metal particles such as Cu particles each having a diameter of about 300 μm, or an Au plating film or an Ag plating film may be formed on an Ni plating film to form a composite plating film.

Further, when a plating target article is made of electrically insulating material such as plastic or the like, a conductive base (primer) forming treatment is carried out as a pre-treatment of the electroplating. However, in the case of a microstructured plating face having a high aspect ratio, an uniform and excellent conductive base could not be formed even if the conductive base forming treatment is carried out by normal electroless plating. Therefore, the thickness of the plating film obtained by the electroplating is liable to be non-uniform. In order to avoid this problem, the conductive base forming treatment may be carried out by sputtering or vacuum deposition. However, in this case, since the treatment is carried out in a pressure-reduced apparatus, there occur such difficulties that the

cost of the treatment apparatus rises up and a mass-production treatment and a continuous treatment cannot be performed. On the other hand, if the conductive base forming treatment using the electroless plating or the like is carried out while vibrational flow is induced in treatment liquid by using the same means as the vibrational flow generating means used in the present invention, a highly uniform conductive base can be formed on even a microstructured plating face having a high aspect ratio. Accordingly, by combining the conductive base forming treatment and the electroplating method of the present invention, the process from the pre-treatment to the electroplating treatment can be continuously carried out, and thus the productivity can be enhanced more and more.

According to the plating method of the present invention, the distribution of the plating bath into microstructure recess portions can be enhanced by the vibrational flow which is induced in the plating bath 14 by the vibrational flow generator 16, and also the uniformity in film thickness can be enhanced by pulsing the plating current density so that a first pulse state and a second pulse state where the pulsed current density has the same polarity as that of the first pulse state although it is sufficiently lower than that of the first state. Therefore, there can be suppressed occurrence of non-uniformity in film thickness due to concentrated plating film formation at the projecting portions or edge portions and also occurrence of defects such as gas pits, etc. in through holes or via holes as in the case of the DC plating process, and high surface glossiness can be achieved. Further, there can be prevented such a phenomenon that a plating film which has been temporarily formed is partially dissolved as in the case of the pulse plating current whose polarity is inverted. Therefore, a high-speed film forming process can be carried out and the construction of the manufacturing apparatus can be simplified. Accordingly, desired plating films can be efficiently formed with low fraction defective at high speed on broad plating target articles.

Further, according to the present invention, short-circuit can be prevented by the action of the vibrational flow occurring in the plating bath 14 even when the distance between the plating target article X and the anode metal member is short to increase the current density. This is considered as a factor to form a plating film with an excellent yield and at high speed without inducing disadvantages such as burning, scorching, etc.

In order to attain such an excellent action, it is remarkably preferable that the three-dimensional flow rate of the vibrational flow of the plating bath 14 is equal to or greater than 150mm per second. Such a high three-dimensional flow rate can be effectively implemented by inducing the vibrational flow in the plating bath. It is difficult to implement this three-dimensional flow rate by using a normal stirrer, and even when it is implemented, an extremely large scale apparatus is needed.

In this embodiment, the effect can be further enhanced by swinging and/or vibrating the plating target article X through the swing and/or vibration of the swinging frame 24. However, an excellent effect can be obtained even when the plating target article X is neither swung nor vibrated. If the cathode bus bar 30, the anode bus bar 32, the plating target article X, the anode metal member, etc. are supported without using the swinging frame 24, the swinging motor 20 and the vibrating motor 28, the construction of the apparatus can be further simplified. When the plating target article X has a plate shape of a relatively large dimension or length as a whole such as a multi-layered wiring board or the like, the effect can be enhanced by swinging the plating target article X along the in-plane direction thereof.

Figs. 9 and 10 are cross-sectional views showing the construction of a plating apparatus to which a second embodiment of the plating method according to the present invention is applied, and Fig. 11 is a plan view showing the plating apparatus shown in Figs. 9 and 10. This embodiment is

different from the first embodiment shown in Figs. 1 to 8 in the way to hold the plating target article X and the way to supply current to the plating target article, and it uses a so-called barrel plating method.

In Figs. 9 to 11, a vibrating frame 44 is fitted to a plating tank 12 through a coil spring 46 as a vibration absorption member. The vibrating frame 44 is fitted to a vibrating motor 48 and a balance weight 49 used to keep a weight balance with the vibrating motor 48. A barrel 52 is fitted to the vibrating frame 44 through a support member 50. The barrel 52 is rotatably fitted to the support member 50, and rotated in the direction indicated by an arrow of Fig. 9 by driving means (not shown). Many minute plating target articles X are accommodated in the barrel 52. Many small holes are formed on the outer peripheral surface of the barrel 52 so that the plating target articles X are prevented from passing through the small holes, but the liquid of the plating bath 14 is allowed to pass through the small holes. A cathode conductive member 54 is disposed in the barrel 52 so as to extend to the lower portion of the barrel 52. The cathode conductive member 54 is connected to a negative-electrode terminal of a power source circuit 34 via an insulated coated wire 54' which passes through a pipe member 52a fixed to the barrel 52 at the rotational center of the barrel 52. The cathode conductive member 54 is not rotated even when the barrel is rotated, and thus the plating target articles X which are rolled through the rotation of the barrel repetitively be in contact with and separate from the cathode conductive member 54.

Reference numeral 56 represents an anode metal member having a lower portion immersed in the plating bath 14. The anode metal member 56 is accommodated in a plastic cage, for example, and is connected to a positive-electrode terminal of the power source circuit 34 through an insulated coated wire 56'. As shown in Fig. 9, the anode metal member 56 is disposed at both the sides of the barrel 52, however, it may be disposed at one side of the anode metal member 56.

The vibrating motor 48 is vibrated at the same amplitude and frequency as the vibrating motor 28 described above, and the plating target articles X are vibrated at an amplitude of 0.05 to 5.0mm, for example 0.1 to 5.0mm, and a vibrational frequency of 100 to 300 revolutions per minute. In this embodiment, the effect is also further enhanced by vibrating the plating target articles through the vibration of the vibrating frame 44. However, an excellent effect can be achieved without vibrating the plating target articles X. The construction of the apparatus can be further simplified by supporting the support member 50 and the barrel 52 without using the vibrating frame 44, the vibrating motor 48, etc.

In this embodiment, the plating current density is set in the same way as described with reference to Fig. 8. In this embodiment, the plating current in the first pulse state or second pulse state or the plating current varying in the shift process between the first pulse state and the second pulse state is supplied to each plating target article X when each plating target article X is brought into contact with the cathode conductive member 54. If only the current density at the contact time is continuously displayed, the same current density as shown in Fig. 8 is obtained on average, and thus the same effect as the first embodiment can be obtained.

This embodiment is more effectively applied to a case where formation of electrode films on plating target articles X having extremely small dimensions, for example, chip parts such as ceramic chip capacitors of about 0.6mm x 0.3mm x 0.2mm in dimension or the like, or formation of plating films on pins of about 0.5mm in diameter x about 20mm in length is carried out on a large number of plating target articles at the same time. As described above, when such a minute article that the dimension in the direction traversing the longitudinal direction, that is, the width is equal to 5mm or less, further 2mm or less, still further 1mm or less is used as the plating target article, the improving effect in the uniformity

of the plating film thickness and the film forming speed is greater. Besides, metal powder alloy, inorganic/organic pigment particulates, metal balls may be targeted as the plating target articles.

As a matter of course, a desired pre-treatment is carried out before the electroplating method of the present invention is carried out. The pre-treatment is carried out in the same manner as the well-known electroplating method.

Further, a vibrational flow generator disclosed in JP(A)-11-189880 (in which vibrating vanes are disposed at the bottom portion of a plating tank, and vibration is transmitted from a vibrating motor through a vibration transmitting frame to the vibrating vanes to vibrate the vibrating vanes in the horizontal direction, as described with reference to Figs. 7 and 8 of this publication) or ones disclosed in publications other than the above publication may be properly used as the vibrational flow generator having the vibrating vanes for generating vibrational flow in the plating path in the method of the present invention.

For example, vibrational flow generators shown in Figs. 21 and 22 may be used. In Figs. 21 and 22, two vibrational flow generators 16 are supported by a support frame 15 fixed to a support stand 13 on which a plating tank 12 is mounted. In each of the vibrational flow generators 16, the upper end portion of a vibration transmitting rod 16e" extending in the up-and-down direction is fixed to a vibrating member 16c' for receiving vibration transmitted from a vibrating motor 16d. The vibration transmitting rod 16e" extends into the plating tank 12, and the end portion of the vibration transmitting rod 16e' in the horizontal direction is fixed to the lower end of the vibration transmitting rod 16e". The vibration transmitting rods 16e' are commonly used by the two vibrational flow generators 16, and vibrating vanes 16f extending in the up-and-down direction are fixed to the vibration transmitting rods 16e'. The vibration is transmitted from the vibrating motors 16d through the vibrating members

16c' and the vibration transmitting rods 16e" and 16e' to the vibrating vanes 16f to vibrate the vibrating vanes 16f in the horizontal direction.

Fig 12 is a cross-sectional view showing another embodiment of the plating apparatus used in the embodiment of the plating method according to the present invention, and Fig. 13 is a partially notched plan view of the plating apparatus of Fig. 12. In this embodiment, the construction of the vibrational flow generator 16 is different from that of the above embodiment. That is, the lower end of a coil spring 16d is fixed to a fixing member 118 fixed to the upper end edge portion of the plating tank 12, and a vibrating motor 16d is fixed to the lower side of a vibrating member 16c to which the upper end of the coil spring 16b is fixed. A lower guide member 124 whose lower end is fixed to the fixing member 118 and an upper guide member 123 whose upper end is fixed to the vibrating member 16c are disposed in the coil spring 16b so as to be spaced from each other at a proper distance.

Figs. 14 and 15 are cross-sectional views of another embodiment of the fixing portion of the vibrational flow generator to the plating tank in the plating apparatus used in the embodiment of the plating method according to the present invention, and Fig. 16 is a plan view of this embodiment. Figs. 14 and 15 are views taken along lines X-X' and Y-Y' of Fig. 16, respectively. In these figures, the cathode, anode, power source circuit, etc. for plating are not shown.

In this embodiment, a laminated member 3 made of a rubber plate 2 and metal plates 1, 1' is used as a vibration absorbing member instead of the coil spring 16b of the above embodiments. The laminated member 3 is formed by fixing the metal plate 1' via a rubber vibration insulator 112 to a support member 118 connected to the upper end of the plating tank 12 by means of a bolt 131, disposing the rubber plate 2 on the metal plate 1', disposing the metal plate 1 on the rubber plate 2, and fixing the metal plates 1, 1' and rubber plate 2 by means of a bolt 116 and nut 117 to be

integrated.

A vibrating motor 16d is fixed to the metal plate 1 via a support member 115 by a bolt 132. The upper end portion of a vibration transmitting rod 16e is connected via a rubber ring 119 to the laminated member 3, especially to the metal plate 1 and rubber plate 2. That is, the upper side metal plate 1 functions as the vibrating member 16c of the embodiment of Fig. 1, etc., and the lower side metal plate 1' functions as the base stand 16a of the embodiment of Fig. 1, etc. The laminated member 3 containing the metal plate 1, 1', especially the rubber plate 2, has the same vibration absorbing function as the coil spring 16b of the embodiment of Fig. 1, etc.

Figs. 17A to 17C show schematic plan views of an embodiment of the laminated member 3. In the embodiment of Fig. 17A corresponding to the above embodiment of Figs. 14 to 16, there is provided a hole 5 through which the vibration transmitting rod 16e passes. In the embodiment of Fig. 17B, the laminated member 3 comprises a first portion 3a and a second portion 3b, the facing edges of which are contacted with each other. According to this embidiment, the vibration transmitting rod 16e can be easily set to the laminated member 3 through the hole 5 thereof when assembling the apparatus. In the embodiment of Fig. 17C, the laminated member 3 is formed so as to have a ring shape corresponding to the shape of the upper edge portion of the plating tank 12, and has an opening 6 positioned at the center thereof.

According to the embodiments of Figs. 17A and 17B, the plating tank 12 is sealed with the laminated member 3, and therefore gas evaporated from the plating bath 14 and plating liquid splashed from the plating bath 14 are prevented from leaking to the environment.

Figs. 18A and 18B show cross-sectional views of the above sealing of the plating tank with the laminated member 3. In the embodiment of Fig. 18A, the sealing of the plating tank 12 is performed by contacting the inner surface of the hole 5 of the rubber plate 2 with the vibration

transmitting rod 16e. In the embodiment of Fig. 18B, there is provided a flexible sealing member 136 attached to the opening 6 of the laminated member 3 and the vibration transmitting rod 16e to seal the space existing therebetween.

Figs. 19A to 19E show examples of the laminated member 3 as the vibration absorbing member. The laminated member 3 of Fig. 19B is the same as that of Figs. 14 to 16. The laminated member 3 of Fig. 19A comprises metal plate 1 and rubber plate 2. The laminated member 3 of Fig. 19C comprises upper metal plate 1, upper rubber plate 2, lower metal plate 1' and lower rubber plate 2'. The laminated member 3 of Fig. 19D comprises upper metal plate 1, upper rubber plate 2, intermediate metal plate 1", lower rubber plate 2' and lower metal plate 1'. The number of the metal plate or rubber plate is 1 to 5 for example. In the present invention, the vibration absorbing member may be formed only of the rubber plate(s).

Examples of material of the metal plates 1, 1', 1" are stainless steel, iron, copper, aluminum, suitable alloys, etc. The thickness of the metal plates 1, 1', 1" is 10 to 40 mm for example. However, the metal plate, for example the intermediate metal plate 1", which is not fixed to any member other than the member constituting the laminated member may be made so thinner as to have the thickness of 0.3 to 10mm for example.

Material of the rubber plate 2, 2' is, for example, synthetic rubber or vulcanized natural rubber, and preferably rubber vibration isolator defined in JIS K6386(1977), especially having static modulus of elasticity in shear of 4 to 22 kgf/cm^2, preferably 5 to 10 kgf/cm^2, and ultimate elongation of 250 % or more.

Examples of synthetic rubber are chloroprene rubber, nitrile rubber, nitrile-chloroprene rubber, styrene-chloroprene rubber, acrylonitrile-butadiene rubber, isoprene rubber, ethylene-propylene-diene rubber, epichlorohydrin rubber, alkylene oxide rubber, fluororubber, silicone rubber, urethane rubber, polysulfide rubber, phosphorus rubber

(flame-retarded rubber). The thickness of the rubber plate is 5 to 60mm for example.

The laminated member 3 of Fig. 19E comprises upper metal plate 1, lower metal plate 1', and rubber plate 2 which comprises an upper solid rubber layer 2a, sponge rubber layer 2b and lower solid rubber layer 2c. One of the upper and lower solid rubber layers 2a, 2c may be omitted. Alternatively, a plurality of sponge rubber layers and a plurality of solid rubber layers may be used in the rubber plate.

Fig. 20 is a graph showing a modification of the variation of the plating current (current density) flowing through the plating target article X due to the voltage applied across the cathode bus bar 30 and the anode bus bar 32 by the power source circuit 34. In this modification, the current density waveforms of the first and second states are not the rectangular form as shown in Fig. 8, but contain a little pulsation as shown in Fig. 20. Such pulsation is based on the construction of the power source circuit 34, and the plating current used in the present invention may be pulsated current as shown in Fig. 20. The peak values in the first and second states may be used as the current values I1 and I2 in the first and second states, respectively.

In the present invention, the power source circuit 34 may comprise a voltage supply system for the first state and another voltage supply system for the second state. In this case, the voltages of these voltage supply systems are alternately output (i.e., this power source circuit is functionally equivalent to the switching operation of two power source devices).

The combination technique of the vibrational flow of the plating bath and the pulsed plating current as described above may be applied to an anodizing method, an electrolytic polishing method, an electrolytic degreasing method, etc. in which the surface treatment of target objects is carried out by utilizing current flow in a treatment bath. The target

objects are disposed at the anode side or cathode side in accordance with the treatment content. By using this combination technique, the surface treatment on target articles having microstructures can be excellently performed.

The present invention will be described in more detail with the following examples.

EXAMPLE 1:

The apparatus described with reference to Figs. 1 to 3 was used. Here, a vibrating motor of 150W x 200V x 3ϕ was used as the vibrating motor 16d, a plating tank having a volume of 300 liters was used as the plating tank 12, and Power Master (available from Chuo Seisakusho, Co., Ltd.) was used as the power source circuit 34.

8-Inch (diameter of 200mm) silicon wafers which were subjected to a predetermined pre-treatment by the conventional method were used as the plating target articles X, and a process of forming copper-embedded conductive film in blind via holes coated with a copper seed layer in the copper damascene method was carried out. Many blind via holes were formed in a titanium nitride insulation layer of 0.35μm in thickness to have an inner diameter of 0.24μm.

The following through hole bath of copper sulfate plating was used as the plating bath 14:

Copper sulfate:	75g/L
Sulfuric acid:	190g/L
Brightener:	proper amount
Chlorine ion:	40mL/L

The vibrating motor 16d of the vibrational flow generator 16 was vibrated at 45Hz to vibrate the vibrating vanes 16f at an amplitude of 0.2mm and a vibration frequency of 650 revolutions per minute in the plating bath 14. Further, the vibrating motor 28 was vibrated at 25Hz to vibrate the plating target articles X at an amplitude of 0.15mm and a

vibration frequency of 200 revolutions per minute in the plating bath 14. The three-dimensional flow rate in the plating bath at this time was measured as 200mm/second by a three-dimensional electromagnetic flowmeter ACM300-A (available from Alec Electronics Co., Ltd.).

The plating current of rectangular waveform was supplied by the power source circuit 34 so that I1, I2, T1, T2 shown in Fig. 8 satisfied I1=6[A/wafer] = 3[A/dm^2], I2=0.6[A/wafer], T1=10[second], T2=1[second].

When the treatment was carried out for 10 minutes, it was found on the basis of a current flowing test, microscopy and other tests that excellent copper plating films of about 10μm in thickness were formed and embedded in all the blind via holes.

<u>COMPARATIVE EXAMPLE 1-1</u>:

The same treatment as Example 1, except for the condition: T2=0[second], was carried out. It was proved from the current flowing test, microscopy and other tests that excellent embedding of copper plating film was carried out in some (58%) of the many blind via holes, however, was not carried out in the other blind via holes.

<u>COMPARATIVE EXAMPLE 1-2</u>:

The same treatment as Example 1, except that the vibrational flow generator 16 was not actuated, was carried out. It was proved from the current flowing test, microscopy and other tests that excellent embedding of copper plating film was carried out in some (10%) of the many blind via holes, however, was not carried out in the other blind via holes (defectives due to burning, scorching or the like occurred).

<u>EXAMPLE 2</u>:

The plating conductive films were formed on the inner surfaces of through holes by using the apparatus described with reference to Figs. 1 to 3 (the vibrating motor 16d, the plating tank 12 and the power source circuit 34 were the same as Example 1) and using as the plating target article X an A4-size multi-layered wiring board which was subjected to the

pre-treatment by the conventional method. Many through holes had an inner diameter of 30μm ϕ and an aspect ratio of 10.

The following normal bath of copper sulfate plating was used as the plating bath 14:

Copper sulfate: 200g/L
Sulfuric acid: 50g/L
Brightener: proper amount
Chlorine ion: 60mL/L

The vibrating motor 16d of the vibrational flow generator 16 was vibrated at 50Hz to vibrate the vibrating vanes 16f at an amplitude of 0.2mm and a vibration frequency of 700 revolutions per minute in the plating bath 14. Further, the vibrating motor 28 was vibrated at 25Hz to vibrate the plating target articles X at an amplitude of 0.15mm and a vibration frequency of 200 revolutions per minute in the plating bath 14. Further, the swinging motor 20 was driven to swing the plating target articles X at a swinging width of 30mm and a swinging frequency of 20 times per minute. The three-dimensional flow rate in the plating bath at this time was measured as 200mm/second by the three-dimensional electromagnetic flowmeter ACM300-A.

The plating current of rectangular waveform was supplied by the power source circuit 34 so that I1, I2, T1, T2 shown in Fig. 8 satisfied I1=4[A/dm^2], I2=0.4[A/dm^2], T1=180[second], T2=20[second].

When the treatment was carried out for 10 minutes, it was found on the basis of a current flowing test, microscopy and other tests that excellent copper plating films were formed in 99.9% through holes.

<u>COMPARATIVE EXAMPLE 2-1</u>:

The same treatment as Example 2, except for the condition: T2=0[second], was carried out. It was proved from the current flowing test, microscopy and other tests that excellent copper plating films were formed over the overall length in some (50%) of the many through holes, however,

no excellent copper plating film was formed in the other through holes.

COMPARATIVE EXAMPLE 2-2:

The same treatment as Example 2, except that the vibrational flow generator 16 was not actuated, was carried out. It was proved from the current flowing test, microscopy and other tests that excellent copper plating films were formed in some (10%) of the many through holes, however, no excellent copper plating film was formed in the other through holes (defectives due to burning, scorching or the like occurred).

EXAMPLE 3:

The apparatus described with reference to Figs. 9 to 11 (the vibrating motor 16d, the plating tank 12 and the power source circuit 34 were the same as Example 1), and 800 ceramic chips of 0.6mm x 0.3mm x 0.2mm in dimension which were subjected to the pre-treatment by the conventional method were used as plating target articles X. Nickel plating films to form electrode films were formed on the end surfaces at both ends of each ceramic chip in the longitudinal direction thereof and on a part (an area located within 0.1mm from both the end surfaces) of the 0.6mm x 0.3mm surface adjacent to the end surfaces.

The following barrel bath was used as the nickel plating bath 14:

Nickel sulfate:	270g/L
Nickel chloride:	68g/L
Boric acid:	40g/L
Magnesium sulfate:	225g/L

The vibrating motor 16d of the vibrational flow generator 16 was vibrated at 55Hz to vibrate the vibrating vanes 16f at an amplitude of 0.2mm and a vibration frequency of 750 revolutions per minute in the plating bath 14. The vibrating motor 48 was vibrated to vibrate the target plating articles at an amplitude of 0.15mm and a vibration frequency of 250 revolutions per minute in the plating bath 14. The three-dimensional flow rate in the plating bath at this time was measured as 210mm/second by the

three-dimensional electromagnetic current meter ACM300-A. The barrel 52 having a mesh opening ratio of 20% was used, and the rotational number of the barrel was set to 10 rpm.

The plating current of rectangular waveform was supplied by the power source circuit 34 so that I1, I2, T1, T2 shown in Fig. 8 satisfied I1=0.4[A/dm^2], I2=0.04[A/dm^2], T1=20[second], T2=2[second].

When the treatment was carried out at 50℃ for 30 minutes, it was found on the basis of a current flowing test, microscopy and other tests that excellent nickel plating films of about 2μm in thickness were formed in all the ceramic chips.

<u>COMPARATIVE EXAMPLE 3-1</u>:

The same treatment as Example 3, except for the condition: T2=0[second], was carried out. It was proved from the current flowing test, microscopy and other tests that excellent nickel plating films were formed in some (12%) of the ceramic chips, however, no excellent nickel plating film was formed in the other ceramic chips.

<u>COMPARATIVE EXAMPLE 3-2</u>:

The same treatment as Example 3, except that the vibrational flow generator 16 was not actuated, was carried out. It was proved from the current flowing test, microscopy and other tests that excellent nickel plating films were formed in some (60%) of the ceramic chips, however, no excellent nickel plating film was formed in the other ceramic chips.

<u>EXAMPLE 4</u>:

In place of the nickel plating, tin plating was carried out in the same way as Example 3. The following sulfate bath of acidic tin plating was used as the plating bath 14:

Stannous sulfate:	50g/L
Sulfuric acid:	100g/L
Cresolsulfonic acid:	100g/L
Gelatin:	2g/L

β-naphthol 1g/L

The plating current of rectangular waveform was supplied by the power source circuit 34 so that I1, I2, T1, T2 shown in Fig. 8 satisfied I1=0.4[A/dm²], I2=0.04[A/dm²], T1=20[second], T2=2[second].

When the treatment was carried out at 50℃ for 60 minutes, it was found on the basis of a current flowing test, microscopy and other tests that excellent tin plating films were formed in all the ceramic chips.

COMPARATIVE EXAMPLE 4-1:

The same treatment as Example 4, except for the condition: T2=0[second], was carried out. It was proved from the current flowing test, microscopy and other tests that excellent tin plating films were formed in some (10%) of the ceramic chips, however, no excellent tin plating film was formed in the other ceramic chips.

COMPARATIVE EXAMPLE 4-2:

The same treatment as Example 4, except that the vibrational flow generator 16 was not actuated, was carried out. It was proved from the current flowing test, microscopy and other tests that excellent tin plating films were formed in some (57%) of the ceramic chips, however, no excellent tin plating film was formed in the other ceramic chips.

EXAMPLE 5:

The apparatus described with reference to Figs. 9 to 11 (the vibrating motor 16d, the plating tank 12 and the power source circuit 34 were the same as Example 1), and 30 brass pins of 0.5mm φ in outer diameter and 20mm in length which were subjected to the pre-treatment by the conventional method were used as plating target articles X. Nickel plating films were formed on the outer surfaces of the pins.

The following barrel bath was used as the nickel plating bath 14:

Nickel sulfate: 270g/L

Nickel chloride: 68g/L

Boric acid: 40g/L

Magnesium sulfate: 225g/L

The vibrating motor 16d of the vibrational flow generator 16 was vibrated at 45Hz to vibrate the vibrating vanes 16f at an amplitude of 0.2mm and a vibration frequency of 500 revolutions per minute in the plating bath 14. The vibrating motor 48 was vibrated to vibrate the target plating articles at an amplitude of 0.15mm and a vibration frequency of 200 revolutions per minute in the plating bath 14. The three-dimensional flow rate in the plating bath at this time was measured as 200mm/second by the three-dimensional electromagnetic current meter ACM300-A. The barrel 52 having a mesh opening ratio of 20% was used, and the rotational number of the barrel was set to 10 rpm.

The plating current of rectangular waveform was supplied by the power source circuit 34 so that I1, I2, T1, T2 shown in Fig. 8 satisfied I1=3[A/dm^2], I2=0.3[A/dm^2], T1=30[second], T2=3[second].

When the treatment was carried out at 50℃ for 20 minutes, it was found on the basis of the measurement of the thickness of the nickel plating films, current flowing test, microscopy and other tests that excellent nickel plating films having excellent uniformity in thickness were formed in all the pins.

<u>COMPARATIVE EXAMPLE 5-1</u>:

The same treatment as Example 5, except for the condition: T2=0[second], was carried out. It was proved from the measurement of the thickness of the nickel plating films, the current flowing test, microscopy and other tests that excellent nickel plating films were formed on some (17%) of the pins, however, no excellent nickel plating film was formed on the other pins.

<u>COMPARATIVE EXAMPLE 5-2</u>:

The same treatment as Example 5, except that the vibrational flow generator 16 was not actuated, was carried out. It was proved from the measurement of the thickness of the nickel plating films, the current

flowing test, microscopy and other tests that excellent nickel plating films were formed in some (60%) of the pins, however, no excellent nickel plating film was formed on the other pins (defectives due to burning, scorching or the like occurred).

EXAMPLE 6:

The apparatus described with reference to Figs. 9 to 11 (the vibrating motor 16d, the plating tank 12 and the power source circuit 34 were the same as Example 1), and about 30000 spheres of acrylonitrile-butadiene-styrene copolymer (ABS resin) each of which had a diameter of 3mm ϕ and was subjected to the pre-treatment (containing a degreasing treatment and a charging treatment) by the conventional method were used as plating target articles X. Copper plating films were formed on the outer surfaces of the spheres.

The following was used as the plating bath 14:

Copper sulfate:	200g/L
Sulfuric acid:	50g/L
Brightener:	proper amount
Chlorine ion:	40mL/L

The vibrating motor 16d of the vibrational flow generator 16 was vibrated at 40Hz to vibrate the vibrating vanes 16f at an amplitude of 0.2mm and a vibration frequency of 700 revolutions per minute in the plating bath 14. The vibrating motor 48 was vibrated to vibrate the target plating articles X at an amplitude of 0.15mm and a vibration frequency of 250 revolutions per minute in the plating bath 14. The three-dimensional flow rate in the plating bath at this time was measured as 210mm/second by the three-dimensional electromagnetic current meter ACM300-A. The barrel 52 having a mesh opening ratio of 20% was used, and the rotational number of the barrel was set to 10 rpm.

The plating current of rectangular waveform was supplied by the power source circuit 34 so that I1, I2, T1, T2 shown in Fig. 8 satisfied

$I1=0.5[A/dm^2]$, $I2=0.04[A/dm^2]$, $T1=30$[second], $T2=3$[second].

When the treatment was carried out at 50℃ for 30 minutes, it was found on the basis of the measurement of the thickness of the copper plating films, current flowing test, microscopy and other tests that excellent copper plating films having excellent uniformity in thickness were formed in 99.5% spheres.

COMPARATIVE EXAMPLE 6-1:

The same treatment as Example 6, except for the condition: $T2=0$[second], was carried out. It was proved from the measurement of the thickness of the copper plating films, the current flowing test, microscopy and other tests that excellent copper plating films were formed in some (40%) of the spheres, however, no excellent copper plating film was formed in the other spheres.

COMPARATIVE EXAMPLE 6-2:

The same treatment as Example 6, except that the vibrational flow generator 16 was not actuated, was carried out. It was proved from the measurement of the thickness of the copper plating films, the current flowing test, microscopy and other tests that excellent copper plating films were formed in some (50%) of the spheres, however, no excellent copper plating film was formed in the other spheres.

EXAMPLE 7:

The apparatus described with reference to Figs. 1 to 3 was used. Here, a vibrating motor of 150W x 200V x 3ϕ was used as the vibrating motor 16d, a plating tank having a volume of 300 liters was used as the plating tank 12, and Power Master PMD1 (available from Chuo Seisakusho, Co., Ltd.) was used as the power source circuit 34.

A silicon wafer having a size of 40mm x 40mm and a thickness of 1mm which was subjected to a predetermined pre-treatment by the conventional method was used as the plating target article X, on the surface of which many blind via holes each having an inner diameter of 20μm and a depth of

$70\mu m$ were formed.

The following through hole bath of copper sulfate plating was used as the plating bath 14:

Copper sulfate: 75g/L
Sulfuric acid: 190g/L
Brightener: proper amount
Chlorine ion: 40mL/L

In the plating tank 12, an aeration tube made of ceramics having an outer diameter of 75 mmϕ, an inner diameter of 50mm ϕ, a length of 500mmm, a pore size of 50 to 60 μm and a porosity of 33 to 38% was disposed to generate air bubbles in the plating bath 14.

The vibrating motor 16d of the vibrational flow generator 16 was vibrated at 40Hz to vibrate the vibrating vanes 16f at an amplitude of 0.1mm and a vibration frequency of 650 revolutions per minute in the plating bath 14. Further, the vibrating motor 28 of 75W x 200V x 3ϕ was vibrated at 25Hz to vibrate the plating target articles X at an amplitude of 0.15mm and a vibration frequency of 200 revolutions per minute in the plating bath 14. The three-dimensional flow rate in the plating bath at this time was measured as 200mm/second by the three-dimensional electromagnetic flowmeter ACM300-A.

The plating current of rectangular waveform was supplied by the power source circuit 34 so that I1, I2, T1, T2 shown in Fig. 8 satisfied I1=1.5[A/wafer], I2=0.1[A/wafer], T1=0.08[second], T2=0.02[second].

When the treatment was carried out for 2.5 hours, it was found on the basis of the current flowing test, microscopy and other tests that copper plating films having a uniform thickness of about $7\mu m$ were formed in all the inner surfaces of the blind via holes.

<u>COMPARATIVE EXAMPLE 7</u>:

The same treatment as Example 7, except for the condition: T2=0[second], was carried out. It was proved from the current flowing test,

microscopy and other tests that the openings of the blind via holes were sealed with the copper plating films.

EXAMPLE 8:

The same treatment as Example 7, except that a high frequency vibrating motor was used as the vibrating motor 16d, the vibrating motor 16d was vibrated at 150Hz to vibrate the vibrating vanes 16f at an amplitude of 0.2mm and a vibration frequency of 1200 revolutions per minute in the plating bath 14, and the treatment time was 1.5 hours.

It was proved from the current flowing test, microscopy and other tests that the copper plating films having a uniform thickness of about 7 μm were formed in all the inner surfaces of the blind via holes.

EXAMPLE 9:

An epoxy resin plate for wiring board was used as the plating target article X, on the surface of which many blind via holes each having an inner diameter of 15 μm and a depth of 40 μm were formed.

As the pre-treatment for the electroplating treatment, degreasing - water washing - etching - water washing - neutralizing - water washing - catalyst - water washing - accelarator - water washing - electroless copper plating were conducted to make the plating target article X electically conductive. Furthermore, water washing - activating - water washing - strike plating were conducted. In the electroless copper plating and strike plating, the vibrational flow was generated in the plating treatment liquid by means of the same vibrational flow generator as described with reference to Figs. 1 to 3.

The electroplating treatment was carried out in the same manner as Example 7, except that the swinging motor 20 was actuated to swing the plating target article X at a swinging width of 30mm and a swinging frequency of 20 times per minute in the plating bath 14. The three-dimensional flow rate in the plating bath was measured as 200mm/second by the three-dimensional electromagnetic flowmeter ACM300-A.

The plating current of rectangular waveform was supplied by the power source circuit 34 so that I1, I2, T1, T2 shown in Fig. 8 satisfied I1=4.5[A/dm^2], I2=0.4[A/dm^2], T1=0.08[second], T2=0.015[second].

When the treatment was carried out for 1 hour, it was found on the basis of the current flowing test, microscopy and other tests that copper plating films were excellently formed and embedded in all the blind via holes.

<u>COMPARATIVE EXAMPLE 8</u>:

The same treatment as Example 9, except for the condition: T2=0[second], was carried out. It was proved from the current flowing test, microscopy and other tests that the openings of the blind via holes were sealed with the copper plating films, however, voids remained in the innermost of the blind via holes.